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Title of the Invention: FLAME RETARDANT SYNTHETIC FIBER
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SPECIFICATION

1. TITLE OF THE INVENTION
FLAME RETARDANT SYNTHETIC FIBER

2. CLAIMS

A flame retardant synthetic fiber that is produced by spinning a thermoplastic resin composition obtained by adding 3 to 80 parts by weight of a high molecular weight halogenated bisphenol A-type phenoxy resin that is an addition reaction product containing as main components halogenated bisphenol A diglycidyl ether and halogenated bisphenol A, and has an epoxy value and a phenolic acid value such that the sum of the epoxy value and the phenolic acid value is 10 (mgKOH/g) or less as well as a halogen content of 20 weight % or more, with respect to 100 parts by weight of a thermoplastic polyester resin and/or a thermoplastic polyamide resin.

3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a flame retardant synthetic fiber, and in particular, to a flame retardant polyester fiber and a flame retardant polyamide fiber obtained by adding a high molecular weight halogenated bisphenol A-type phenoxy resin.

Fibers composed mainly of a thermoplastic polyester resin such as polyethylene terephthalate and polybutylene terephthalate, and fibers

composed mainly of a thermoplastic polyamide resin such as nylon 6 and nylon 66 have excellent properties and have been used in all fields both for clothing and industrial purposes.

Meanwhile, from the viewpoint of fire prevention, as the demand for ensuring the safety of fiber products from fire grows, these fibers are required to have flame retardancy.

Various methods have been proposed to allow a polyester fiber and a polyamide fiber, which are flammable, to have flame retardancy. The most commonly used method is as follows. A fiber or a fiber product is subjected to an after-treatment with a flame retardant compound containing halogen, phosphorus, nitrogen, sulfur, or the like, thereby allowing the fiber or the fiber product to have flame retardancy. However, the effect achieved by this method is transitory, and the added flame retardant drops off relatively easily through washing, dry cleaning, and the like, resulting in a decreased flame retardant effect. On the other hand, a method in which a flame retardant monomer component containing halogen or phosphorus is copolymerized is expected to achieve a permanent flame retardant effect. However, this method has the disadvantage that significant coloring occurs under high-temperature reaction conditions, and the molecular weight is less likely to be increased during polymerization, resulting in a large decrease in physical properties. Further, there is a method in which a flame retardant is kneaded in a step after the start of polymerization and before spinning. In this method, if the flame retardant is insoluble in a resin, it is likely to cause unfavorable phenomena such as clogging of a filter and single yarn breakage during spinning. Even if the flame retardant is soluble in a resin, it causes sublimation, bleeding, decomposition, and the like during spinning when it is of low molecular weight. There is an attempt to increase the flame retardant in molecular weight, which, however, leads to disadvantages such as an adverse effect on the melt viscosity of a polymer compatible with a resin, a decrease in the physical properties of the polymer, and intense melting and dropping during burning of a spun fiber or a fiber product. Under the circumstances, there is no

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practical flame retardant.

In view of the above-described various disadvantages in allowing a polyester fiber and a polyamide fiber to have flame retardancy, the present inventors studied intensively for a flame retardant synthetic fiber free from the above-described disadvantages, and found a highly useful polymer-type flame retardant that is well compatible with a resin, and causes little adverse effect on melting and physical properties, no sublimation, and no bleeding onto a fiber surface when allowing a thermoplastic polyester resin or polyamide resin to have flame retardancy, as a result of which the present invention was achieved.

More specifically, the present invention provides a flame retardant synthetic fiber that is produced by spinning a thermoplastic resin composition obtained by adding 3 to 80 parts by weight of a high molecular weight halogenated bisphenol A-type phenoxy resin that is an addition reaction product containing as main components halogenated bisphenol A diglycidyl ether and halogenated bisphenol A, and has an epoxy value and a phenolic acid value such that the sum of the epoxy value and the phenolic acid value is 10 (mgKOH/g) or less as well as a halogen content of 20 weight % or more, with respect to 100 parts by weight of a thermoplastic polyester resin and/or a thermoplastic polyamide resin.

The thermoplastic polyester used in the present invention is a linear high molecular weight polyester obtained from aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, orthophthalic acid, naphthalenedicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-diphenyl ether dicarboxylic acid, α,β-bis(4-carboxyphenoxy)ethane, and 5-sodium sulfoisophthalic acid or ester-forming derivatives thereof; and glycols such as ethylene glycol, propylene glycol, butanediol, pentanediol, neopentylglycol, hexanediol, octanediol, decanediol, cyclohexanedimethanol, hydroquinone, bisphenol A, 2,2-bis(4-hydroxyethoxyphenyl)propane, and tetrabromobisphenol A-ethylene oxide adduct. Particularly preferable polyester is polyethylene terephthalate and polybutyrene terephthalate. The polyester may contain a small proportion of aliphatic carboxylic acids

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such as adipic acid, sebacic acid, decanedicarboxylic acid, and cyclohexanedicarboxylic acid; hydroxycarboxylic acids such as glycolic acid, hydroxy-butyric acid, hydroxybenzoic acid, and naphthyl glycolic acid; polyalkylene ether glycols such as polyethylene glycol and polytetramethylene glycol; lactone compounds such as butyrolactone, valerolactone, and caprolactone; or multifunctional ester-forming components such as trimethylolpropane, trimethylolethane, glycerin, pentaerythritol, trimellitic acid, trimesic acid, and pyromellitic acid within a range capable of maintaining thermoplasticity.

The thermoplastic polyamide resin used in the present invention is a resin containing an amide group, which is obtained from ring-opening polymerization products of lactams, polycondensation products of diamines and dibasic acids, self-polycondensation products of w-amino acids, or copolymers thereof. Specific examples include all well-known polyamides such as polycapramide, polylauramide, polyhexamethylene adipamide, polyhexamethylene sebacamide, polyhexamethylene lauramide, polyxylylene adipamide, or copolymers thereof. Particularly preferable polyamide is polycapramide (nylon 6) and polyhexamethylene adipamide (nylon 66). The polyamide resin used in the present invention contains, along with an amide group, a linking group such as an ester group, an ether group, an urethane group, an imide group, a urea group, a carbonate group, a ketone group, an acid anhydride group, and a sulfone group, which may be formed into a random polymer, a block copolymer, or a graft copolymer with the amide component, or have a network structure in a range having thermoplasticity. Thus, examples also include polyetheramide, polyesteramide, polyamide imide, elastomer-modified polyamide, and the like.

On the other hand, the high molecular weight halogenated bisphenol A-type phenoxy resin is used as a flame retardant component for the thermoplastic resin composition used in the present invention. The halogenated bisphenol A as a main component thereof is obtained by replacing a part or all of hydrogen atoms of a benzene nucleus by chlorine or

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bromine atoms.　Examples thereof include
2,2-bis(4-hydroxy-3-chlorophenyl)propane,
2,2-bis(4-hydroxy-3-bromophenyl)propane,
2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane,
2,2-bis(4-hydroxy-3,5-dibromophenyl)propane,
2,2-bis(4-hydroxy-2,3,5-trichlorophenyl)propane,
2,2-bis(4-hydroxy-2,3,5-tribromophenyl)propane,
2,2-bis(4-hydroxy-2,3,5,6-tetrachlorophenyl)propane, and
2,2-bis(4-hydroxy-2,3,5,6-tetrabromophenyl)propane.

The high molecular weight halogenated bisphenol A-type phenoxy resin can be obtained as follows, for example.　A mixture obtained by mixing halogenated bisphenol A diglycidyl ether obtained by condensation between the above-described halogenated bisphenol A and epichlorohydrin and halogenated bisphenol A so as to have a halogen content of 20 weight % or more is heated to 80°C to 250°C in the presence of a catalyst, and caused to react so that the sum of an epoxy value and a phenolic acid value is 10 (mgKOH/g) or less.　At this time, in a range ensuring a halogen content of 20 weight % or more, another bifunctional epoxy compound, phenol compound, hydroxy compound, and dicarboxylic acid, such as bisphenol A diglycidyl ether, diphenyl sulfone diglycidyl ether, tetrabromodiphenyl sulfone diglycidyl ether, 1,6-hexanediglycidyl ether, bisphenol A, dihydroxydiphenyl sulfone, tetrabromodiphenyl sulfone, 1,6-hexanediol, and isophthalic acid may be used in combination and denatured.

This kind of reaction can be performed in a common reaction vessel. However, there is a tendency for the melt viscosity of the phenoxy resin to increase sharply with its degree of polymerization, which makes it more difficult to perform a production operation.　In view of this, a reaction vessel of a heat carrier heating type intended for a highly viscous resin is used in general.

In order to produce the phenoxy resin more rationally, the following methods summarized as described below may be adopted.　Consequently, it would be possible to obtain the composition of the present invention more

easily and reliably.

(1) First, both components of the halogenated bisphenol A (if necessary, bisphenol A may be used in combination; this also applies to the following) and the halogenated bisphenol A diglycidyl ether to be reacted are preliminarily reacted in a common reaction vessel until the most advantageous reaction rate in production is reached. Then, the resultant preliminary reactant is kneaded with a kneader such as a single-screw or multi-screw extruder, a coneader, and a heating roller, followed by the reaction.

(2) Second, both components of the halogenated bisphenol A and the halogenated bisphenol A diglycidyl ether to be reacted are preliminarily reacted in a common reaction vessel in the same manner as in (1) above, resulting in a preliminary reactant. The preliminary reactant is moved into another vessel or place that enables the easy removal of the content, followed by the reaction under a predetermined warming condition.

(3) Third, a halogenated bisphenol A-type phenoxy resin having a halogen content of 20 weight% or more and a terminal epoxy group as represented by the following general formula I, which is obtained by condensation between the halogenated bisphenol A and the halogenated bisphenol A diglycidyl ether, and a halogenated bisphenol A-type phenoxy resin having a halogen content of 20 weight% or more and a terminal OH group as represented by the following general formula II, which is obtained by a reaction between the halogenated bisphenol A diglycidyl ether and the halogenated bisphenol A, are kneaded together with a kneader such as a single-screw or multi-screw extruder, a coneader, and a heating roller, followed by the reaction. Further, the resultant product is aged if necessary.

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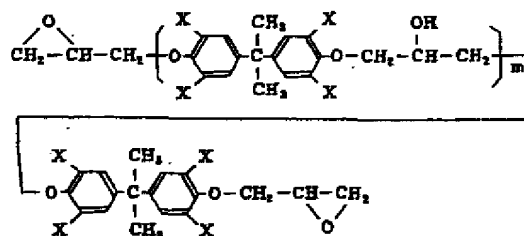
(Formula I)

where X represents a H, Cl, or Br atom, and m is an integer or decimal ranging from 1.5 to 10 at an average degree of polymerization.

(Formula II)
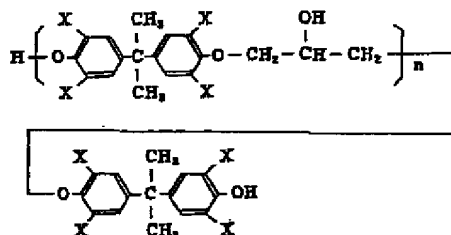
where X represents a H, Cl, or Br atom, and n is an integer or decimal ranging from 1.5 to 10 at an average degree of polymerization.

At this time, a color protection stabilizer may be added if necessary.

Quantities of a phenolic hydroxyl group and an epoxy group as a terminal functional group of the high molecular weight halogenated bisphenol A-type phenoxy resin used in the present invention are determined by the following methods.

(1)   Quantitative determination of phenolic acid value

25 g of a mixed solvent of toluene and benzyl alcohol at a weight ratio of 2:1 is added to 3 g of a halogenated bisphenol A-type phenoxy resin, followed by heating and melting at 100°C. Then, the resultant solution is titrated with 1/10 N alcoholic KOH with phenolphthalein as an indicator, and the phenolic acid value is calculated based on the following formula.

$$\text{Phenolic acid value (mgKOH/g)} = \frac{5.610 \times A \times F}{W} \times 1000$$

A: Amount (ml) of 1/10 N alcoholic KOH required for neutralization

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F: Titer of 1/10 N alcoholic KOH

W: Weight (g) of sample

(2)   Quantitative determination of epoxy value

      5 ml of a solution of hydrochloric acid and pyridine at a volume ratio of 16:484 and 100 g of benzyl alcohol are added to 3 g of a halogenated bisphenol A-type phenoxy resin, and the resultant solution is refluxed for 20 minutes while being stirred at times.   Then, unreacted pyridium chloride is back-titrated with 1/10 N alcoholic KOH with phenolphthalein as an indicator still under a warming condition, and the epoxy value is calculated based on the following formula.

$$\text{Epoxy value (mgKOH/g)} = \frac{5.610 \times (B+C-T) \times F}{W} \times 1000$$

B: Amount (ml) of 1/10 N alcoholic KOH required for blank test

C: Amount (ml) of 1/10 N alcoholic KOH required for neutralizing sample

T: Amount (ml) of 1/10 N alcoholic KOH required for back titration

F: Titer of 1/10 N alcoholic KOH

W: Weight (g) of sample

      When halogenated bisphenol A diglycidyl ether having a terminal epoxy group, such as tetrabromobisphenol A diglycidyl ether [epoxy value: 171 (mgKOH/g)] and halogenated bisphenol A having a terminal phenolic OH group, such as tetrabromobisphenol A [phenolic acid value: 206 (mgKOH/g)] are reacted, the epoxy group and the phenolic OH group are consumed and decreased as polymerization proceeds.   Thus, a remaining amount of the epoxy group and the phenolic OH group is an indicator of an increase in molecular weight.

      The high molecular weight halogenated bisphenol A-type phenoxy resin used in the present invention is a high molecular weight material having an epoxy value of 10 (mgKOH/g) or less and a phenolic acid value of 10 (mgKOH/g) or less such that the sum of the epoxy value and the phenolic acid value is 10 (mgKOH/g) or less.   If the epoxy value and the phenolic acid value of the phenoxy resin are larger than 10, in other words, the

phenoxy resin is of lower molecular weight, the phenoxy resin bleeds onto a fiber surface and is eliminated through washing and the like, resulting in a gradually decreasing flame retardant effect. In particular, if the epoxy value is large, it becomes difficult to perform stable spinning due to an increased melt viscosity of a thermoplastic resin composition to which the halogenated phenoxy resin has been added, a partially produced gel, and the like. On the other hand, if the phenolic acid value is large, a fiber is likely to be thermally colored. Thus, both the cases result unfavorably.

It is advantageous that the high molecular weight halogenated bisphenol A-type phenoxy resin has a higher content of halogen in terms of fiber properties, because this makes it possible to decrease the amount of adding the phenoxy resin to the polyester resin or the polyamide resin. The halogen content is preferably 20 weight% or more, and particularly preferably 30 to 70 weight%.

The high molecular weight halogenated bisphenol A-type phenoxy resin has a terminal epoxy group or a terminal phenolic OH group, which may be blocked by carbon acids, alcohols, phenols, amines, isocyanates, or the like to form modified materials.

The use amount of the phenoxy resin as a flame retardant component is appropriately in a range of 3 to 80 parts by weight (hereinafter, abbreviated simply as "parts"), and preferably 5 to 50 parts with respect to 100 parts of the polyester resin or the polyamide resin. If the use amount is less than 3 parts, a sufficient flame retardant effect cannot be obtained. On the other hand, if the use amount is more than 80 parts, the strength and thermal properties of a flame retardant fiber are decreased. Thus, both the cases result unfavorably.

Although the high molecular weight halogenated bisphenol A-type phenoxy resin may be added alone to achieve a flame retardant effect, a flame retardant aid that synergistically enhances flame retardancy may be used in combination if necessary. Typical examples of the flame retardant aid include antimony trioxide, antimony pentoxide, sodium pyroantimonate, tin dioxide, zinc metaborate, aluminium hydroxide, zirconium oxide,

molybdenum oxide, and the like.   Although antimony oxide is a flame retardant aid having a high flame retardant synergistic effect, it enhances thermal decomposition when used in combination with polyethylene terephthalate.   Thus, consideration should be given to the use amount, the dispersion state, the melt spinning condition, and the like.

In producing the flame retardant synthetic fiber of the present invention, other additives such as a crystal nucleating agent, a pigment, a dye, a plasticizer, a lubricant, an antistatic agent, a heat-resisting stabilizer, an antioxidant, and an ultraviolet absorber may be used.   Further, another flame retardant or another type of polymer may be used in combination.

The flame retardant, the flame retardant aid, or the various additives may be added at any stage between the start of producing polyester or polyamide and spinning.   However, a stage after the end of polymerization and before melt spinning is appropriate.

The flame retardant may be added by being incorporated directly into a polymer, followed by melt spinning, by being melted uniformly into pellets, followed by spinning, or by incorporating a previously prepared high level masterbatch of the flame retardant, followed by melt spinning.

A melt spinning method for obtaining the flame retardant synthetic fiber of the present invention is not defined particularly, and a well-known method is applicable.

In spinning, the flame retardant may be dispersed uniformly in a polymer, or alternatively, a core-in-sheath structure may be adopted in which a polymer layer containing no flame retardant wraps a core of a polymer containing a high level of the flame retardant like a sheath.

The flame retardant polyester fiber and the flame retardant polyamide fiber obtained by the present invention have excellent enduring flame retardancy, and can be used widely for clothing, curtains, carpets, wall covering cloths, car interior materials, industrial fibers, and the like.

The following is a specific description of the present invention, with reference to reference examples, examples, and a comparative example.   In the following, "parts" and "%" refer to "parts by weight" and "weight%",

respectively, unless otherwise specified.

In a burning test described in the examples, a flame retardant fabric sample that incorporates a glass fiber was attached to a U-shape holder in accordance with an oxygen index (LOI) method [JIS K-7201] that expresses a measurement as a minimum oxygen concentration required for a material to keep on burning.

Reference Example 1 (example of preparing high molecular weight brominated bisphenol A-type phenoxy resin)

740 parts of tetrabromobisphenol A diglycidyl ether having an epoxy equivalent of 370, 495 parts of tetrabromobisphenol A, and 0.6 parts of a solution containing 10% of tetramethylammonium chloride were put into a flask, and caused to react at 150°C for 3 hours and at 180°C for 2 hours. Then, the resultant product was taken out onto a tray to be cooled and solidified. Thereafter, the solidified product was pulverized into pale yellow powder.

The product thus obtained had a softening point of 130°C with an epoxy value (mgKOH/g; this also applies to the following) of 40 and a phenolic acid value (mgKOH/g; this also applies to the following) of 28.

Next, 1.0 parts of tetramethylammonium chloride was mixed with respect to 1000 parts of this product, and the mixture was caused to react further at 200°C with an extruder having a single-screw vent measuring 50 mm in diameter, while the number of revolutions of the screw was adjusted so that the resin stays within the extruder for 2 minutes.

Thereafter, a high molecular weight tetrabromobisphenol A-type phenoxy resin obtained through cooling and solidification was pulverized into pale yellow powder.

The resin thus obtained had a softening point of 190°C with an epoxy value of 5.5 and a phenolic acid value of 2.5, the sum of which was 8.0, and a bromine content of 52.5%.

Further, the flow rate (g/10 minutes; this also applies to the following) of this objective resin at 200°C was measured in accordance with

ASTM D-1238, which resulted in 4.4.

Reference Example 2 (example of preparing brominated phenoxy resin for comparison)

A treatment was performed in the same manner as in Reference Example 1 except that 290 parts of tetrabromobisphenol A and 1.0 parts of the tetramethylammonium chloride solution were used and that the reaction at 180°C was performed for 4 hours, which resulted in a pale yellow tetrabromobisphenol A-type phenoxy resin for comparison that had a softening point of 125°C with an epoxy value of 45 and a phenolic acid value of 1.0, the sum of which was 46, a bromine content of 52%, and a flow rate of 250.

Example 1

25 parts of the high molecular weight tetrabromobisphenol A-type phenoxy resin obtained in Reference Example 1 was mixed uniformly with respect to 100 parts of polyethylene terephthalate having an intrinsic viscosity of 0.65 (measured at 25°C with a solvent of orthoclorophenol), and the mixture was melt and extruded with a single-screw extruder having a Dulmage screw set at 270°C to 280°C to be made into pellets. Each of the pellets was melt spun with a screw-type extruding spinning machine set at 270°C to 280°C, and then drawn to 3.5 times its original length, resulting in a monofilament of 75 denier. Spinning was performed stably with no sublimation of the flame retardant observed and no single yarn breakage and the like occurring due to clogging. The physical properties, i.e., the strength and elongation at break of the monofilament were 4.6 g/denier and 27%, respectively. As a result of performing a burning test, a fabric composed of blank filaments was flammable with an oxygen index (LOI) of 20, whereas a fabric composed of the filaments of the present example had a LOI value of 29, ranking as flame retardancy. Further, the fabric composed of the filaments of the present example was washed with trichlene at room temperature for 3 hours, resulting in no change in weight, and thus proved

to have excellent resistance to dray cleaning.

Example 2

20 parts of the high molecular weight tetrabromobisphenol A-type phenoxy resin obtained in Reference Example 1 and 5 parts of antimony trioxide were mixed uniformly with respect to 100 parts of polybutylene terephthalate having an intrinsic viscosity of 0.8 (measured at 30°C with a solvent of phenol and tetrachloroethane at a ratio of 6:4), and the mixture was melt and extruded with a single-screw extruder having a Dulmage screw set at 250°C to be made into pellets. Each of the pellets was melt spun with a screw-type extruding spinning machine set at 250°C, and then drawn to 3.5 times its original length, resulting in a monofilament of 75 denier. Spinning was performed stably with no sublimation of the flame retardant, no single yarn breakage, and the like observed as in Example 1.

As a result of performing a burning test, a fabric composed of the filaments of the present example had a LOI value of 32 (a fabric composed of blank filaments had a LOI value of 21), ranking as flame retardancy. Further, the fabric showed no extraction weight loss due to trichlen, and thus was proved to have excellent resistance to dray cleaning.

Comparative Example 1

Melting and extrusion were performed in the same manner as in Example 1 except that the tetrabromobisphenol A-type phenoxy resin obtained in Reference Example 2 was used instead of the phenoxy resin of Reference Example 1, thereby obtaining pellets. When each of the pellets was melt spun at 270°C to 280°C, an increased melt viscosity and single yarn breakage due to a produced gel were observed. Due to a failure to obtain stable spinning workability, it was impossible to perform spinning for a long time.

Example 3

100 parts of pellets of nylon 6 (average molecular weight: about

20000) and 30 parts of the high molecular weight tetrabromobisphenol A-type phenoxy resin obtained in Reference Example 1 were treated in the same manner as in Example 1 (except that the temperature condition was 260°C), resulting in a flame retardant nylon monofilament of 75 denier. Spinning was performed stably with no trouble.

As a result of performing a burning test, a fabric composed of blank filaments had a LOI value of 22, whereas a fabric composed of the filaments of the present example had a LOI value of 29, ranking as flame retardancy. Further, the flame retardant was hardly eluted from the fabric composed of the filaments of the present example through washing and dry cleaning.

Example 4

100 parts of pellets of nylon 6 (average molecular weight: about 20000), 30 parts of the high molecular weight tetrabromobisphenol A-type phenoxy resin obtained in Reference Example 1, and 20 parts of antimony trioxide were treated in the same manner as in Example 1 (except that the temperature condition was 260°C), resulting in a flame retardant nylon monofilament of 75 denier. Spinning was performed stably with no trouble.

As a result of performing a burning test, a fabric composed of the filaments of the present example had a LOI value of 33 (a fabric composed of blank filaments had a LOI value of 22), ranking as flame retardancy. Further, the flame retardant was hardly eluted from the fabric composed of the filaments of the present example through washing and dry cleaning.